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## Far Infrared Absorption in Liquefied Gases

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### **Far Infrared Absorption in Liquefied Gases**

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# FAR INFRARED ABSORPTION IN LIQUEFIED GASES \*

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## ABSTRACT

Experimental results are given for the absorption coefficient of the liquids hydrogen (three para concentrations), nitrogen, oxygen, carbon monoxide, methane and argon in the wavenumber range  $20\text{-}250\text{ cm}^{-1}$  ( $40\text{-}500\text{ }\mu\text{m}$ ). In addition, data for liquid hydrogen are given at wave numbers up to  $600\text{ cm}^{-1}$  ( $16.7\text{ }\mu\text{m}$ ). The results are discussed in terms of the induced dipole, and, in the case of carbon monoxide, the permanent dipole. An indication of the way in which the data may be employed in calculations of thermal radiative transfer is made by calculation of the modified Planck mean absorption coefficient.

Key Words: Far infrared; absorption coefficient; liquefied gases; hydrogen; nitrogen; oxygen; carbon monoxide; methane; argon.

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## 1. INTRODUCTION

Absorption spectra of simple molecules in the far infrared are generally related to rotational transitions. For transitions involving permanent dipole moments the effect of increase of density is to broaden the rotational lines. However, at sufficiently high densities absorption also occurs in non-polar species where none had been apparent at low densities. Such absorption is well known (e.g. Bosomworth and Gush, 1965) and is attributed to electric dipole moments induced on collision by the quadrupole and higher multipole fields of neighboring molecules. It is conveniently studied at liquid densities where path lengths of a few centimeters are sufficient for observation. Unfortunately, as with other phenomena dependent on collisions none of the theory of induced absorption is applicable at these densities so that the resulting spectra do not yield molecular constants (e.g. quadrupole moments). Nevertheless, because the spectra result exclusively from the molecular interactions of the liquid state it was felt that an exploratory investigation of several simple molecular species would be useful apart from the value of such reference data as might result.

In this report we present the far infrared spectra of liquids hydrogen (three different para-hydrogen concentrations), nitrogen, oxygen, methane, and carbon monoxide. In addition, we have examined liquid argon in our absorption cell and verified that within the uncertainty limits of our experiments it does not absorb. Since the work involved the solution of several problems peculiar to this type of measurement we give a fairly full account of experimental details (sections 2 and 3). In section 4 the experimental results are presented and discussed and in section 5 we indicate briefly the application of the data in calculations of thermal radiative transfer.

## 2. EXPERIMENTAL

### 2.1 The Spectrophotometer

The spectrophotometer could be used with conventional globar or high pressure mercury lamp sources, crystal choppers, reststrahlen and wire mesh reflection filters. The monochromator had an aperture ratio of  $f/3.8$  and used Littrow mounted gratings in first order in a single pass arrangement. The detector was a Golay cell. In all measurements reported here the instrument was used in single beam operation using a lock-in amplifier to drive a chart recorder with reference signal taken from a breaker on the chopper drive (see figure 1.) For all measurements the instrument was kept purged with dry nitrogen gas from a boiling liquid nitrogen reservoir.

### 2.2 Optical Dewar and Liquid Absorption Cells.

A special dewar, figure 2, was constructed to enable liquid cells to be held at predetermined temperatures. In all experiments liquid hydrogen was used as refrigerant in the inner container and a liquid cell was attached at the lower end of the reflux tube — a thin-walled stainless steel tube passing through the refrigerant container. Variable thermal conductance between the refrigerant and the liquid cell could be obtained by variation of hydrogen gas pressure inside the reflux tube. The liquid cell was surrounded by a nitrogen-temperature radiation shield except for holes to allow the passage of the spectrophotometer beam. When liquid hydrogen was used as sample, a second hydrogen-temperature shield attached to the refrigerant bath was used. The outer vacuum jacket of the dewar was fitted with 1/8" thick polyethylene windows.

Two choices of window are available in the far infrared, namely: crystal quartz and polyethylene. Polyethylene is desirable on account



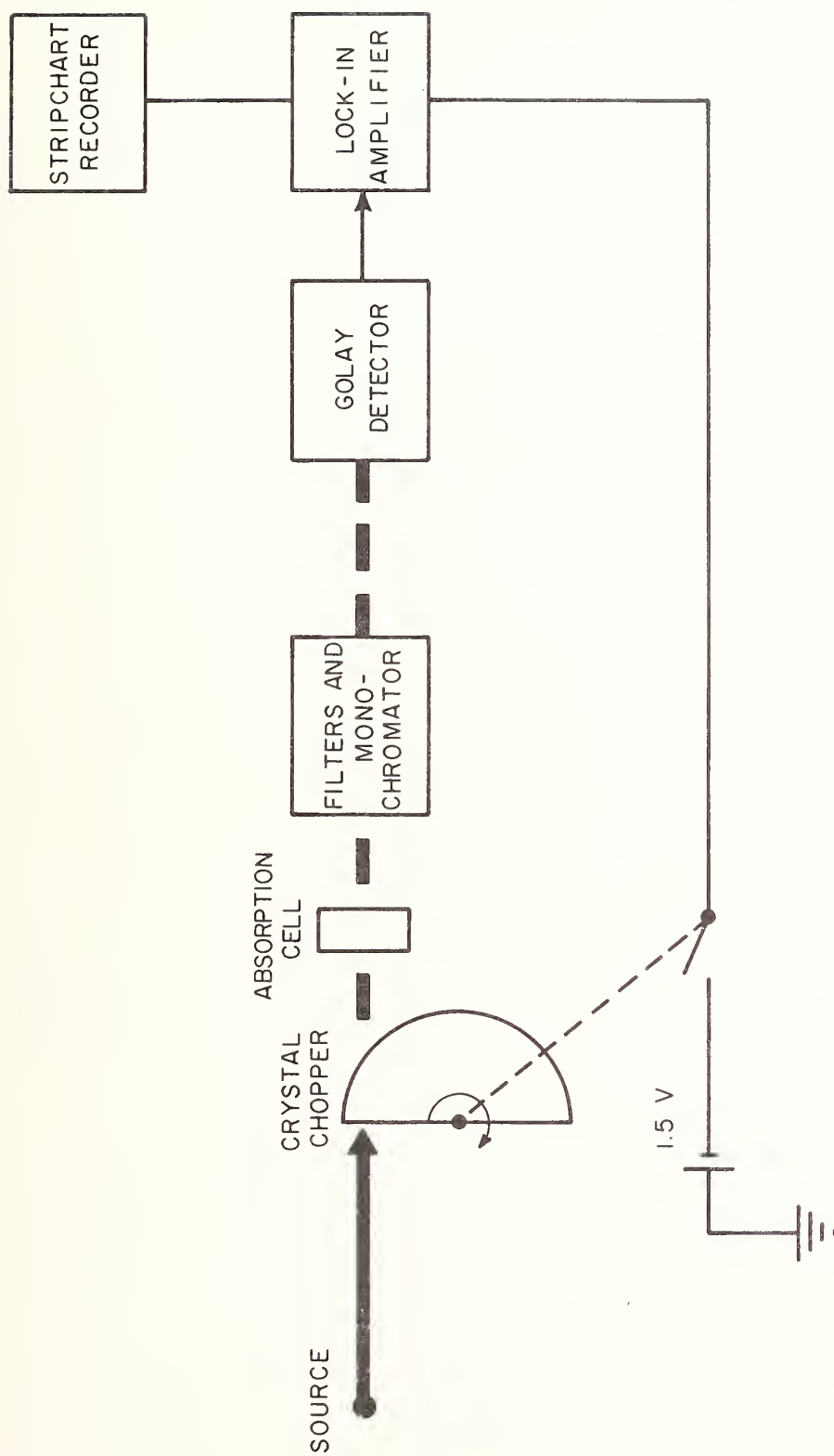


Figure 1. Schematic Arrangement.

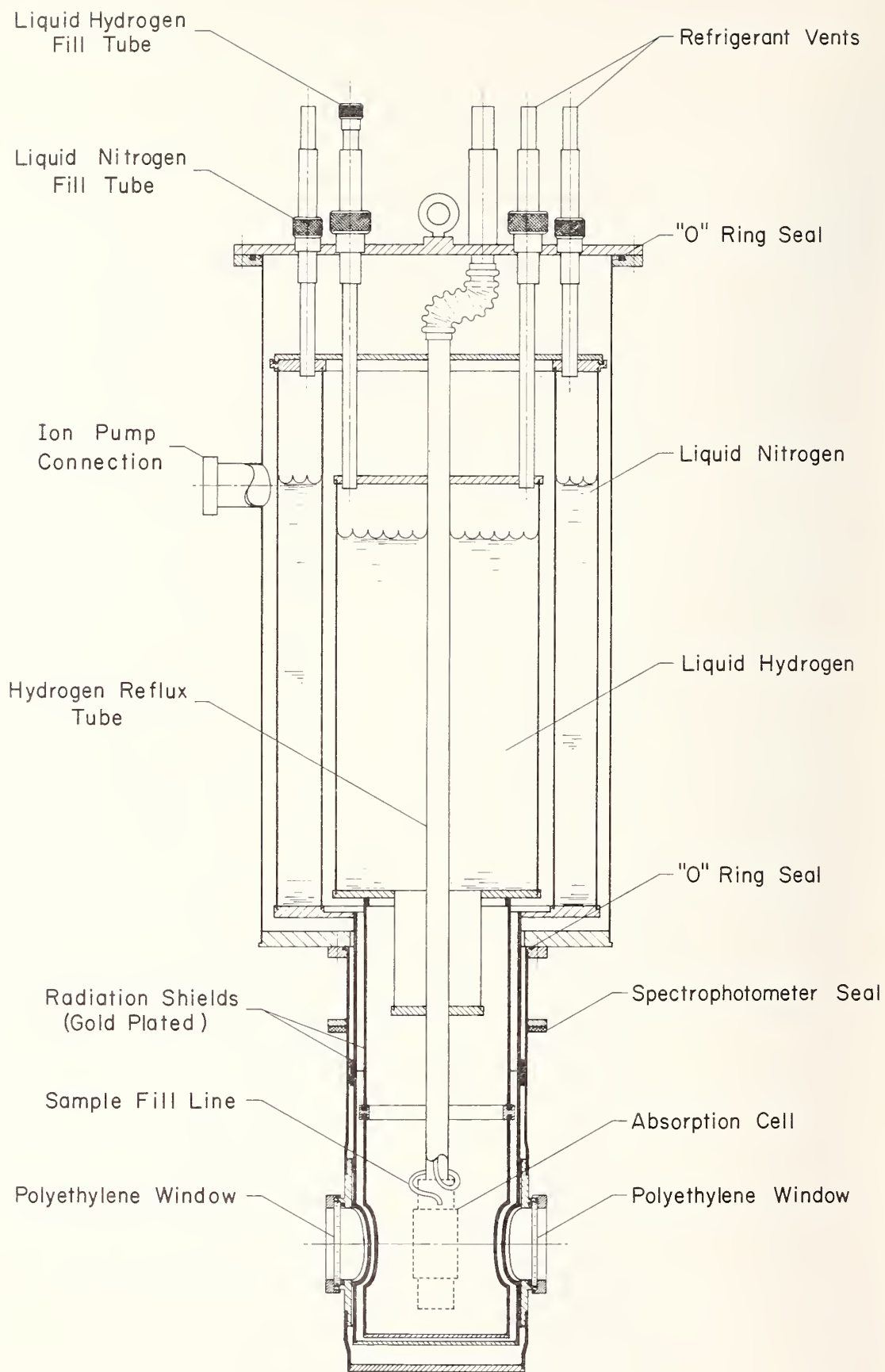


Figure 2. Optical Dewar.

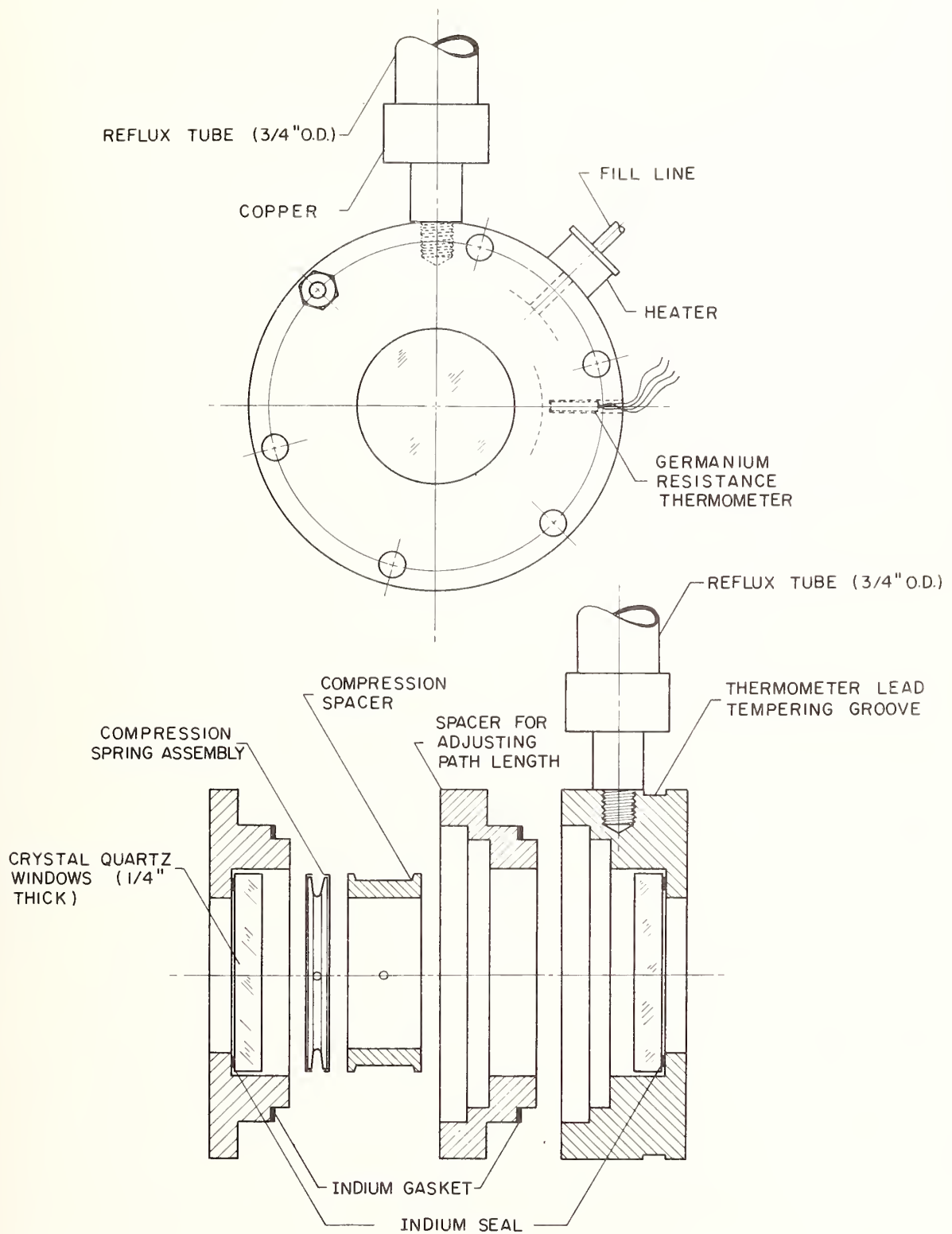


Figure 3. Absorption Cell-Quartz Windows. Path Length Variable from 4.1 mm to 25.4 mm.

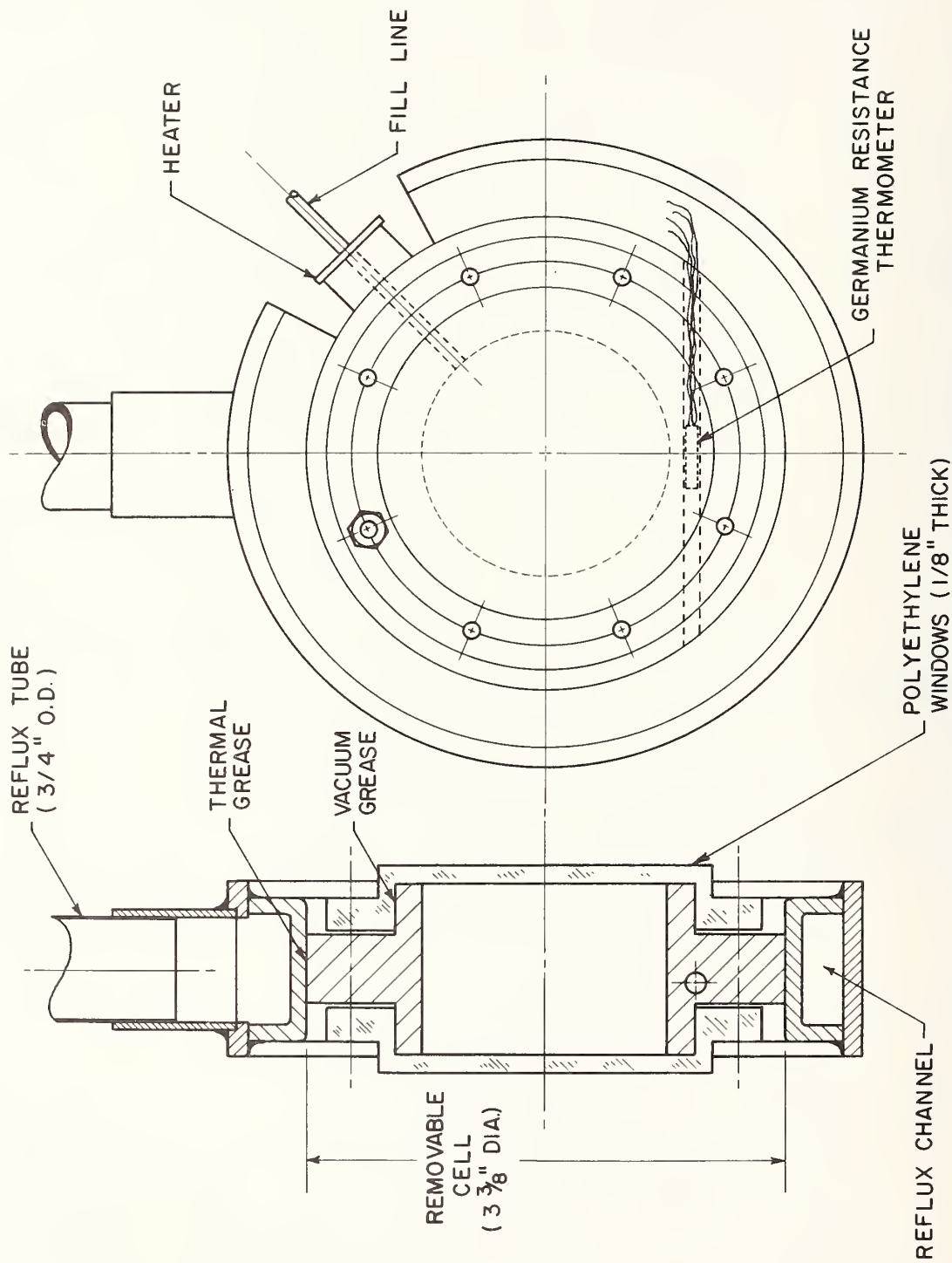


Figure 4. Absorption Cell-Polyethylene Windows. Path Length 32.5 mm. The Cell is Shown Inserted in the Reflux Channel Yoke.

of its wide spectral range as a window ( $0$  to  $600\text{ cm}^{-1}$ ) and again on account of the low reflectance loss at a polyethylene/vacuum interface (about 5%). However, it is less satisfactory than quartz where window rigidity is important. Our earlier attempts at making vacuum tight low temperature liquid cells with polyethylene windows were, however, unsuccessful due to its excessive shrinkage on cooling, and so experiments were begun using the cell of figure 3. This cell was fitted with crystal quartz windows cut perpendicular to the x or y axes. Crystal quartz is readily sealed using indium wire as a gasket material. However, we found that a spring load on the seal was required to maintain the seal through temperature cycles. This was achieved by use of the 'U' cross section steel spring ring shown in the figure. With it a force of 200 pounds was continually maintained against the window seal. The path length of this cell could be changed from 12.7 to 25.4 mm by the inclusion of the spacer shown. For an even shorter path length, 4.1 mm, one window could be raised by including a spacer between window and seat.

The cell of figure 3 was used for all experiments on liquids nitrogen, oxygen, methane, carbon monoxide, and argon and some preliminary runs with hydrogen. It had a usable wave number range from  $0$  to  $250\text{ cm}^{-1}$  and an almost constant reflectance of 15 percent was measured at a vacuum/quartz interface in this range.

For measurements on liquid hydrogen, where much of the interest is at wave numbers beyond  $250\text{ cm}^{-1}$ , we eventually designed a successful polyethylene window seal and this is embodied in the cell shown in figure 4. This cell had a path length of 32.5 mm and could be used where the absorption coefficient was less than about  $1\text{ cm}^{-1}$ . The polyethylene windows are forced over the drum forming the cell body with vacuum grease as sealant. On cooling down, the outer flange



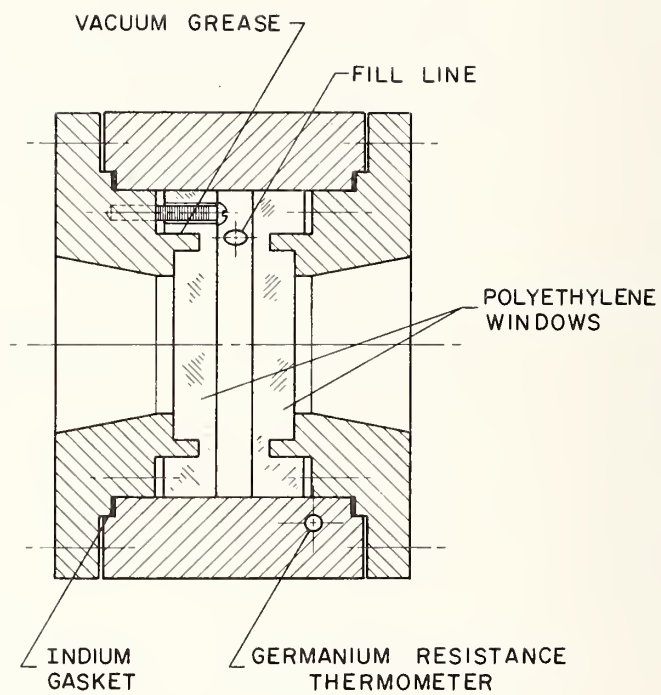


Figure 5. Absorption Cell-Polyethylene Windows. Path Length 5.9 mm.

shrinks on to the drum forming an ever tighter seal. Whereas the cell of figure 3 could be simply screwed to the end of the reflux tube, in order to obtain low enough temperatures for hydrogen liquid samples in this cell we found it necessary to extend the reflux tube in the form of a channel around the cell. The cell body then simply slides into the yoke formed by this channel. Thermal contact with the channel was maintained by use of a zinc-oxide-filled silicone grease.

For short path lengths and higher pressures the design of figure 5 was used in which the same window sealing principle is embodied, but now pressure in the cell acts to seal it further. This cell can also be slid into the reflux channel yoke of figure 4. The path length was 5.9 mm.

All cells were fitted with a single 1/8" diameter copper fill line, a 40  $\Omega$  heater and a well to receive a germanium resistance thermometer bulb. When liquid hydrogen was to be condensed into a cell, the fill time was shortened considerably by routing the fill line down through the reflux tube, thereby precooling the incoming gas before it entered the cell. For all other samples, the fill line remained on the outside of the radiation shields.

### 2.3 Thermometry and Temperature Control

Temperatures of the sample cells were measured with the germanium resistance thermometer. This had received a manufacturer's calibration, but due to the irreproducibility of the resistance we checked it against temperatures obtained by measuring vapor pressures of sample liquids in half filled cells. This was done with liquids nitrogen methane and hydrogen. From our vapor pressure determinations we feel that temperatures quoted are within 0.1 K, which is sufficient for these experiments.

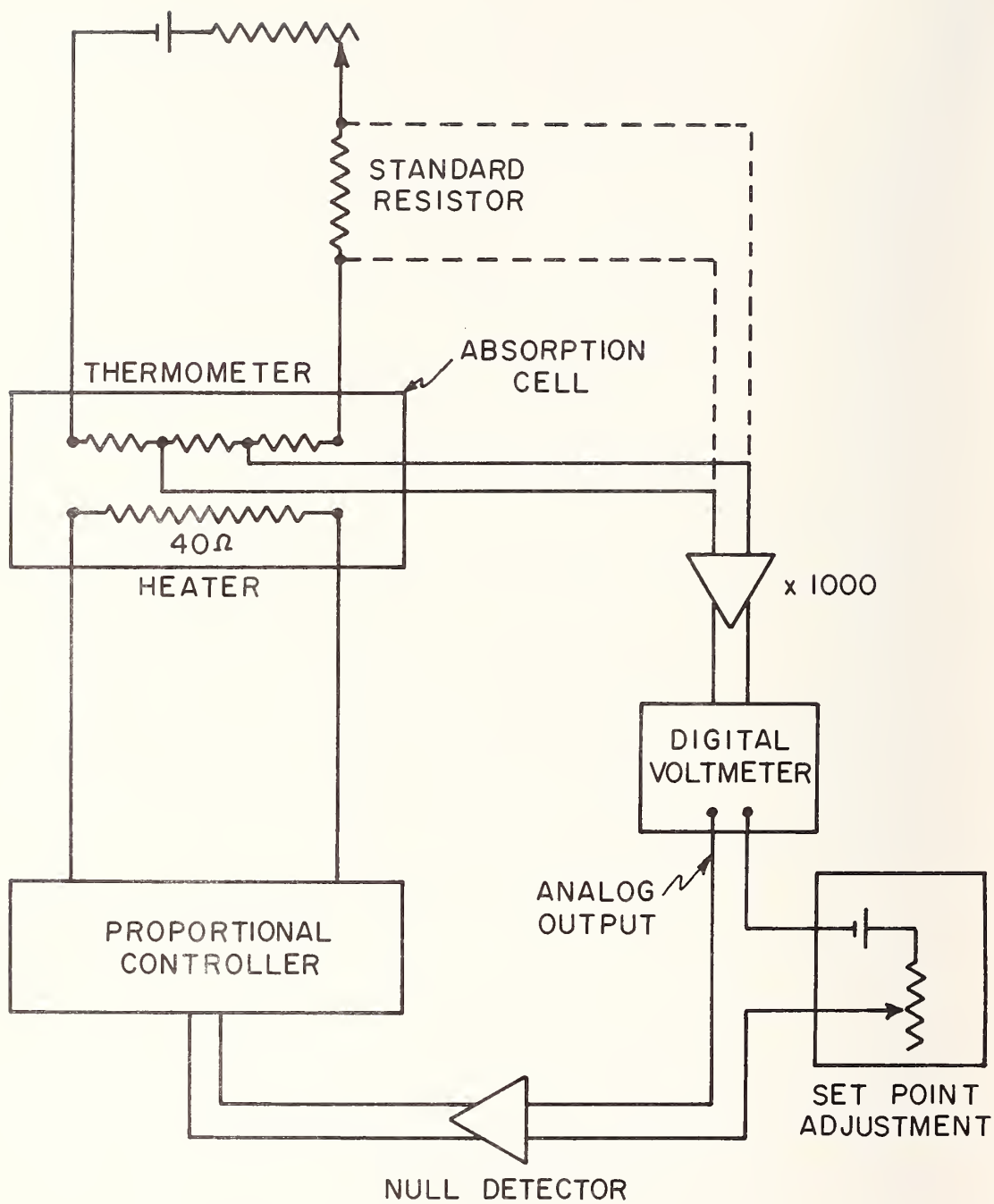


Figure 6. Temperature Measurement and Control System.

Much more important than the absolute value of the temperature itself when using quartz windows in the cell is the stability of the cell temperature. The transmission of the quartz is quite temperature sensitive above about 25 K so it is necessary to make transmission measurements with cell empty and cell full at temperatures within about 0.1 K of each other. With the control system shown schematically in figure 6, control within a few hundredths of a degree was easily achieved. The same thermometer as is used to indicate temperature via the amplifier and digital voltmeter is also used to drive the controller by making use of an isolated analog output of the digital voltmeter.

## 2.4 Liquid Samples

All samples, regardless of their origin were passed through a synthetic zeolite bed at room temperature before entering the cell to guard against possible moisture inclusion.

Normal hydrogen was obtained from a gas cylinder which was known to have been filled several years previously with para-hydrogen from storage boil-off gas. Such cylinders are known to be as pure as the best commercial high purity hydrogen.

Para-hydrogen was obtained from the boil-off of our refrigerant. Its composition was found with a thermal conductivity analyzer to be identical to samples which had been prepared by passing normal hydrogen over an iron oxide catalyst at 20 K and is therefore considered to be essentially equilibrium hydrogen at 20 K, i.e., 99.8 percent parahydrogen.

An intermediate concentration of parahydrogen was obtained by passing normal hydrogen through an iron oxide catalyst held in a liquid nitrogen bath. This method produced a composition which varied

somewhat with flow rate as determined on the thermal conductivity analyzer. At the flow rates used in filling our liquid cell a composition of from 44 to 48 percent parahydrogen was indicated.

Nitrogen was obtained as boil-off gas from commercial liquid for which the manufacturers analysis showed a typical purity of 99.997 percent.

Oxygen, methane, carbon monoxide, and argon were all obtained from cylinders with manufacturers purity specifications of 99.5, 99.95, 99.5, and 99.996 percent respectively.

## 2.5 Experimental Procedure

Prior to taking data, the dewar was placed in the spectrophotometer and with all power on the assembly was allowed to reach steady operating conditions.

With the absorption cell evacuated and cooled down to the required temperature, the transmitted signal was recorded for each of about 8 frequencies. At each frequency the signal was recorded when steady for up to five minutes with suitable filtering (up to a time constant of 100 secs). After this the sample gas was admitted to the cell and condensed in. This process was monitored by both gas flow rate and by continuously recording the signal at a particular frequency; the signal reduced until the beam became completely submerged.

When gas flow had stopped the cell was returned to its original temperature and the signal recorded again at each of the chosen frequencies. On conclusion, the cell was evacuated and again returned to its original temperature to check the original cell empty readings. Readings were repeated unless the cell empty readings agreed to within 2 percent.



Finally, at each of the amplifier gain settings used, the signal was recorded with the spectrophotometer slit closed. This was necessary due to the tendency of the Golay cell to pick up mechanical vibration from the chopper and breakers, which being in constant phase relation to the light signal, appear as a false signal. The resulting offset from the recorder zero is thus a function of the amplifier gain setting.

### 3. RESULTS

#### 3.1 Data Reduction

In deriving the absorption coefficient,  $\alpha$ , from the recorded signals one must take into account the phenomenon of dielectric mismatch at the window/liquid and window/vacuum interfaces and the resulting multiple reflections between pairs of parallel interfaces. In our case the multiple reflections would not give rise to observable interference effects as may easily be shown.

The resonant condition for parallel interfaces separated by a distance  $d$  is

$$d = \frac{m\lambda}{2}$$

where  $m$  is an integer and  $\lambda$  the wavelength. For adjacent resonant wavelengths

$$\frac{\Delta \left( \frac{1}{\lambda} \right)}{\Delta m} = \frac{1}{2d}, \quad \Delta m = 1$$

In our experiments the smallest value of  $d$  was about 3 mm, therefore resonance separation  $\Delta \left( \frac{1}{\lambda} \right)$  is about  $1.6 \text{ cm}^{-1}$  at the most. Most of the data reported here were taken with a spectral slit width approaching  $10 \text{ cm}^{-1}$  so that each recorded signal represents an average of several resonances and none would be observed.

The total intensity at the detector may be calculated by summing the intensities from every possible path through the cell. Referring to figure 7, let  $E_{ijk}$  and  $I_{ijk}$  be the amplitude and intensity of an emerging ray from a path in which there were  $i$  double reflections inside the first window,  $j$  double reflections between the windows and  $k$  double reflections inside the second window. Let  $E_0$  and  $I_0$  be the incident amplitude and intensity respectively and let the amplitude transmission coefficients be  $t_{01}$  for a vacuum/window interface,  $t_{12}$  for a window/liquid interface and  $t_{21}$  and  $t_{10}$  the corresponding coefficients for the reverse order of the media. With the same subscript notation  $r_{lm}$  represents the appropriate amplitude reflection coefficient. Then for a general ray the transmitted amplitude is

$$E_{ijk} = E_0 t_{01} (r_{10} r_{12})^i t_{12}^2 r_{21}^{2j} e^{-(2j+1)\frac{\alpha}{2}\ell} t_{21} (r_{12} r_{10})^k t_{10} \quad (1)$$

The contribution to the intensity from this ray is

$$I_{ijk} = E_0^2 t_{01}^2 (r_{10} r_{12})^{2i} t_{12}^2 r_{21}^{4j} e^{-(2j+1)\alpha\ell} t_{21}^2 (r_{12} r_{10})^{2k} t_{10}^2 \quad (2)$$

The total intensity transmitted through the cell is obtained by summing over  $i$   $j$  and  $k$  from zero to infinity:

$$I_T = \sum_i \sum_j \sum_k I_{ijk} \quad (3)$$

or

$$\frac{I_T}{I_0} = \frac{t_{01}^2 t_{12}^2 t_{21}^2 t_{10}^2 e^{-\alpha\ell}}{(1-r_{10}^2 r_{12}^2) (1-r_{21}^4 e^{-2\alpha\ell}) (1-r_{10}^2 r_{12}^2)} \quad (4)$$

The transmittances  $T$  and reflectances  $R$  at the interfaces can now be introduced and related to the transmission coefficients via the refractive indices,  $n$ , as follows:

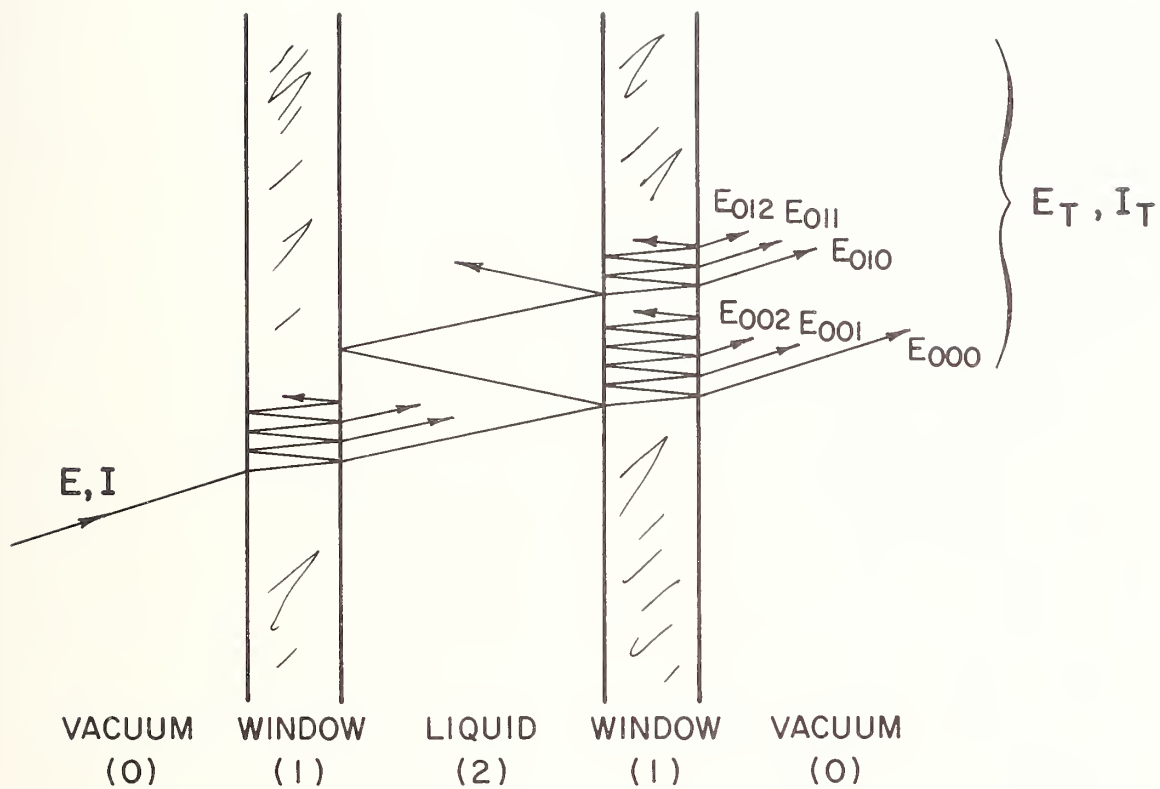


Figure 7. Schematic of Possible Paths Through a Typical Absorption Cell.

$$T_{01} = \frac{n_1}{n_0} t_{01}^2, \quad T_{12} = \frac{n_2}{n_1} t_{12}^2 \quad (5)$$

$$T_{21} = \frac{n_1}{n_2} t_{21}^2, \quad T_{10} = \frac{n_0}{n_1} t_{10}^2$$

Whereas for the reflectances

$$R_{10} = r_{10}^2, \quad R_{12} = r_{12}^2 \text{ etc.} \quad (6)$$

We note also that  $T_{01} = 1 - R_{01}$  etc. The refractive index ratios all cancel upon substitution of (5) and (6) into (4) giving

$$\frac{I_T}{I_0} = \frac{\left(1 - R_{10}\right)^2 \left(1 - R_{12}\right)^2 e^{-\alpha \ell}}{\left(1 - R_{10} R_{12}\right)^2 \left(1 - R_{12}^2 e^{-2\alpha \ell}\right)} \quad (7)$$

The corresponding transmitted intensity  $I'_T$  for the evacuated cell is immediately obtained from (7) on replacing the subscript 2 by 0 giving

$$\frac{I'_T}{I_0} = \frac{\left(1 - R_{10}\right)^4}{\left(1 - R_{10}^2\right)^2 \left(1 - R_{10}^2\right)} \quad (8)$$

On dividing (7) by (8) and taking logarithms

$$\alpha = \frac{1}{\ell} \left\{ \ln \left[ \frac{\left(1 - R_{12}\right)^2 \left(1 - R_{10}^2\right)^2 \left(1 - R_{10}^2\right)}{\left(1 - R_{10}\right)^2 \left(1 - R_{10} R_{12}\right)^2 \left(1 - R_{12}^2 e^{-\alpha \ell}\right)} \right] + \ln \frac{I'_T}{I_T} \right\} \quad (9)$$

An approximation to (9) differing in cases of interest by about 1% is the following

$$\alpha = \frac{1}{\ell} \left\{ \ln \left[ \frac{\left(1 - R_{12}\right)^2 \left(1 - R_{10}^2\right)^2}{\left(1 - R_{10}\right)^2 \left(1 - R_{10} R_{12}\right)^2} \right] + \ln \frac{I'_T}{I_T} \right\} \quad (10)$$

This formula was used in the reduction of data. Its suitability was checked by comparing the resulting absorption coefficient of liquid nitrogen with that obtained from data at two different path lengths. In this case, for path length  $\ell_1$ , we have from equations (7) and (8)

$$\frac{I_{T,1}}{I'_{T,1}} = \frac{(1-R_{12})^2 (1-R_{10}^2)^2 (1-R_{10}^2) e^{-\alpha \ell_1}}{(1-R_{10} R_{12})^2 (1-R_{12}^2 e^{-2\alpha \ell_1}) (1-R_{10})^2} \quad (11)$$

Similarly, for path length 2

$$\frac{I_{T,2}}{I'_{T,2}} = \frac{(1-R_{12})^2 (1-R_{10}^2)^2 (1-R_{10}^2) e^{-\alpha \ell_2}}{(1-R_{10} R_{12})^2 (1-R_{12}^2 e^{-2\alpha \ell_2}) (1-R_{10})^2} \quad (12)$$

On dividing (11) by (12)

$$\frac{I_{T,1}}{I'_{T,1}} \frac{I'_{T,2}}{I_{T,2}} = e^{-\alpha (\ell_1 - \ell_2)} \cdot \frac{(1-R_{12}^2 e^{-2\alpha \ell_2})}{(1-R_{12}^2 e^{-2\alpha \ell_1})} \quad (13)$$

Again, the quotient on the right hand side of equation (13) is very close to unity regardless of the value of  $\alpha$  so that, in this case, the data reduction formula would be

$$\alpha = \frac{1}{\ell_1 - \ell_2} \ln \frac{I'_{T,1} I_{T,2}}{I_{T,1} I'_{T,2}} \quad (14)$$

The absorption coefficient of liquid nitrogen was calculated from equation (10) for data from a path length of 25.4 mm and from equation (14) for data from path lengths of 25.4 mm and 4.1 mm. With



the absorption coefficient reaching a maximum value of  $1.1 \text{ cm}^{-1}$  a maximum discrepancy of  $0.03 \text{ cm}^{-1}$  resulted between the two methods. This was considered to be within experimental error and so the less tedious approach of measurement at a single path length was adopted for all other liquids. It may be appreciated that any error involved is of less consequence with polyethylene windows with their lower refractive index than with quartz.

In order to use equation (10) data were required for the various reflectances involved. The reflectance of the quartz windows in a vacuum was measured in a separate apparatus at liquid nitrogen temperature; the reflectance of high density polyethylene was calculated from published figures (MIT, 1957) for the dielectric constant using the Fresnel equation for normal incidence. Since polyethylene, like quartz, has a low absorption coefficient throughout the far infrared it is sufficient to use microwave measurements of the dielectric constant,  $\epsilon$ , and to assume a frequency independent refractive index. However a correction must be made for low temperatures on account of the large temperature dependence of density (Corruccini and Gniewek, 1961). This was done assuming invariance of the Clausius-Mossotti function,  $\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{\rho}$ , with changes in density.

To calculate the reflectance at a window/liquid interface, it is necessary to know the relative refractive index of the window material to the liquid. Again the absolute refractive index of all liquids measured could be obtained from published values of the microwave or d.c. dielectric constant (Stewart, 1964; Guillien, 1938; Werner and Keesom, 1926; van Itterbeek and Spaepen, 1943; and McLennan, et al., 1930) since these are all weakly absorbing materials. The absolute refractive index of the quartz was calculated from its reflectance while that for polyethylene we already had from its dielectric constant.

### 3.2 Errors

Systematic errors in calculating the absorption coefficient arise from non-linearity of the detector-amplifier-recorder system, from scattered light, and from errors in path length measurement. Non-linearity has been checked and found to be within 0.3 percent. Scattered light is a function of frequency and can best be checked by measuring the transmitted signal of a sample at a frequency where complete extinction is known to occur. However, a randomly selected test frequency does not exhaust the possibilities for scattered light.

Some indication of scattered light was available from two of our experimental runs in which complete extinction occurred. In the first, parahydrogen gave complete extinction at  $390\text{ cm}^{-1}$  in a path length of 32.5 mm. At this frequency, the signal could not be distinguished from that with slits closed and the scattered light is therefore estimated to be less than 0.3 percent. However, because of the width of the parahydrogen absorption peak, this figure conservatively only applies to that component of the scattered light arising from incomplete filtering of higher order radiation, i.e., radiation of higher frequencies reflected by the grating in second and higher orders.

A second run in which complete extinction occurred was with liquid methane in the frequency range 70 to  $250\text{ cm}^{-1}$  in a path length of 25.4 mm. In this range scattered light was generally less than 1 percent although an occasional point as bad as 6 percent appeared. Again this was a very broad ( $\sim 200\text{ cm}^{-1}$ ) band and conclusions must be conservatively limited to higher order radiation.

Our findings are in general agreement with the manufacturer's specifications which state that scattered light is less than 1 percent between 32 and  $665\text{ cm}^{-1}$  except in the region 165 to  $200\text{ cm}^{-1}$  where it approaches but does not exceed 4 percent. Between 20 and  $32\text{ cm}^{-1}$

the manufacturer gives an upper limit of 10 percent.

Path length measurements were made at room temperature with the aid of a micrometer. The major uncertainties in path length arise from shrinkage on cooling down to sample temperature and from the fact that, being in a converging-diverging beam, the infrared rays do not in general follow an axial path through the cell. The total uncertainty in path length from these causes is considered to be less than 1 percent.

Random errors in the recorded signal are by far the more serious. The situation was aggravated by the long period between recording signals with cell empty and cell full, usually as long as 1-1/2 hours. In the frequency region above  $32\text{ cm}^{-1}$ , fluctuations in the signal of about  $\pm 2$  percent occurred in a period of five to ten minutes. Below  $32\text{ cm}^{-1}$  fluctuations were often as great as 20 percent. It is normally not possible to average such long term fluctuations.

For all points where absorption did not exceed 50 percent the combined errors amount to 7 percent in the absorption coefficient calculated from equation (4) for frequencies above  $32\text{ cm}^{-1}$ . Below  $32\text{ cm}^{-1}$  the data must be regarded as of qualitative interest only. Unfortunately peak absorptions for nitrogen and hydrogen were recorded as high as 90 percent in the path lengths available. In this case the error is dominated by the scattered light problem, but an upper limit of 15 percent can be set.

The experimental absorption coefficients are plotted against wave number (reciprocal wavelength) in units of  $\text{cm}^{-1}$ . Wave number repeatability is estimated to be better than  $1\text{ cm}^{-1}$ . A recent check of the manufacturers calibration of the gratings was made by recording drum readings at which higher order images of the mercury green line were incident on the exit slit of the monochromator. A worst

systematic error of  $3\text{ cm}^{-1}$  was recorded, while for most of the spectrum it was less than  $1\text{ cm}^{-1}$ . The error is hardly significant for the broad bands recorded here, particularly since the spectral slit width was sometimes as high as  $10\text{ cm}^{-1}$ .

#### 4. DISCUSSION

The molecular species investigated in this work have one thing in common: they are of zero or low polarity (carbon monoxide has a small permanent electric dipole moment; oxygen has an even smaller magnetic dipole moment. With these two exceptions they show no infrared absorption spectra in the gaseous state at low pressures. At higher pressures, say, of the order of 100 atmospheres, some of the far infrared spectra observed are qualitatively similar to those observed here (Bosomworth and Gush, 1965) and it is fairly well established that they have their origin in collision-induced dipoles. This has one undesirable consequence: as with other properties dependent on collisions there is no theory applicable at densities encountered in the liquid state. At this stage, therefore, a discussion must remain fairly qualitative.

Our data for liquid hydrogen at wave numbers between 20 and  $250\text{ cm}^{-1}$  are new as are those for liquids oxygen, carbon monoxide and methane. The far infrared spectrum of liquid nitrogen and that part of the spectrum of liquid hydrogen above  $300\text{ cm}^{-1}$  have been published previously (Stone and Williams, 1965 and Kiss, 1959).

##### 4.1 Liquid Hydrogen

The spectrum of liquid hydrogen is the most interesting since it consists of two distinct parts each of which is strongly dependent on the ortho-para composition. The weak band below  $250\text{ cm}^{-1}$  (figure 8) is discussed elsewhere (Jones, 1969). It is considered to be a

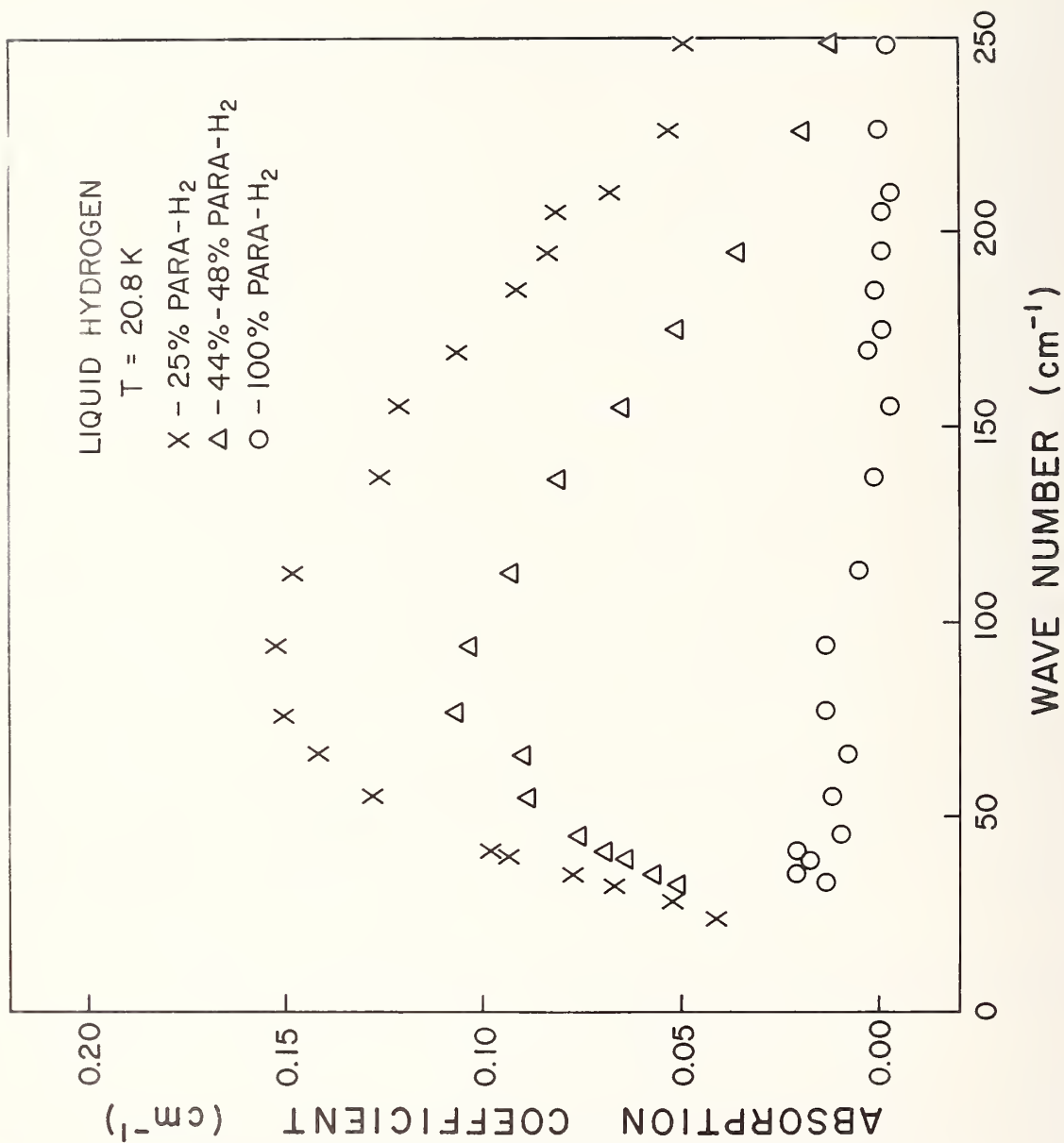


Figure 8. Far Infrared Absorption in Liquid Hydrogen-Translational Band.



translational band and its intensity is roughly linear with the concentration of ortho molecules in accordance with theory. Above  $300\text{ cm}^{-1}$  (figure 9) is a strong band having a peak at  $390\text{ cm}^{-1}$ . This has been identified previously as arising from the pure rotational transition from the state  $J=0$  to  $J=2$  of the para molecules (Kiss 1959). We were unfortunately not able to record the second maximum observed by Kiss at about  $600\text{ cm}^{-1}$  attributable to the ortho transition  $J=1\rightarrow3$  since this was the high frequency limit of our polyethylene windows.

The results of Kiss differ slightly from the present results. While the  $J=0\rightarrow2$  band is of typically Lorentzian shape in our case — although somewhat asymmetric — Kiss's spectrum shows a pronounced shoulder close to the low density Raman frequency of  $354\text{ cm}^{-1}$  (Stoicheff, 1957). Furthermore, Kiss also gives spectra for the solid and then the shoulder becomes a very narrow line ( $<4\text{ cm}^{-1}$  width) shifted only  $1.2\text{ cm}^{-1}$  from the Raman frequency. Apparently our resolution was poorer and we were not able to show the two components of this band, namely: a pure rotational line and a translational summation band according to Kiss.

A discrepancy also exists in the value of the maximum absorption coefficient at  $390\text{ cm}^{-1}$ . For para-hydrogen our peak absorption is some 40% higher while for normal hydrogen it is 30% lower than Kiss's results. These discrepancies are well outside our estimate of experimental uncertainty and remain unexplained.

#### 4.2 Liquid Nitrogen

Our spectrum for liquid nitrogen (figure 10) is quite similar to that obtained by Stone and Williams differing only in the magnitude of the peak absorption coefficient. The values of  $1.08$  and  $1.66\text{ cm}^{-1}$  respectively differ by far more than the total uncertainty estimated

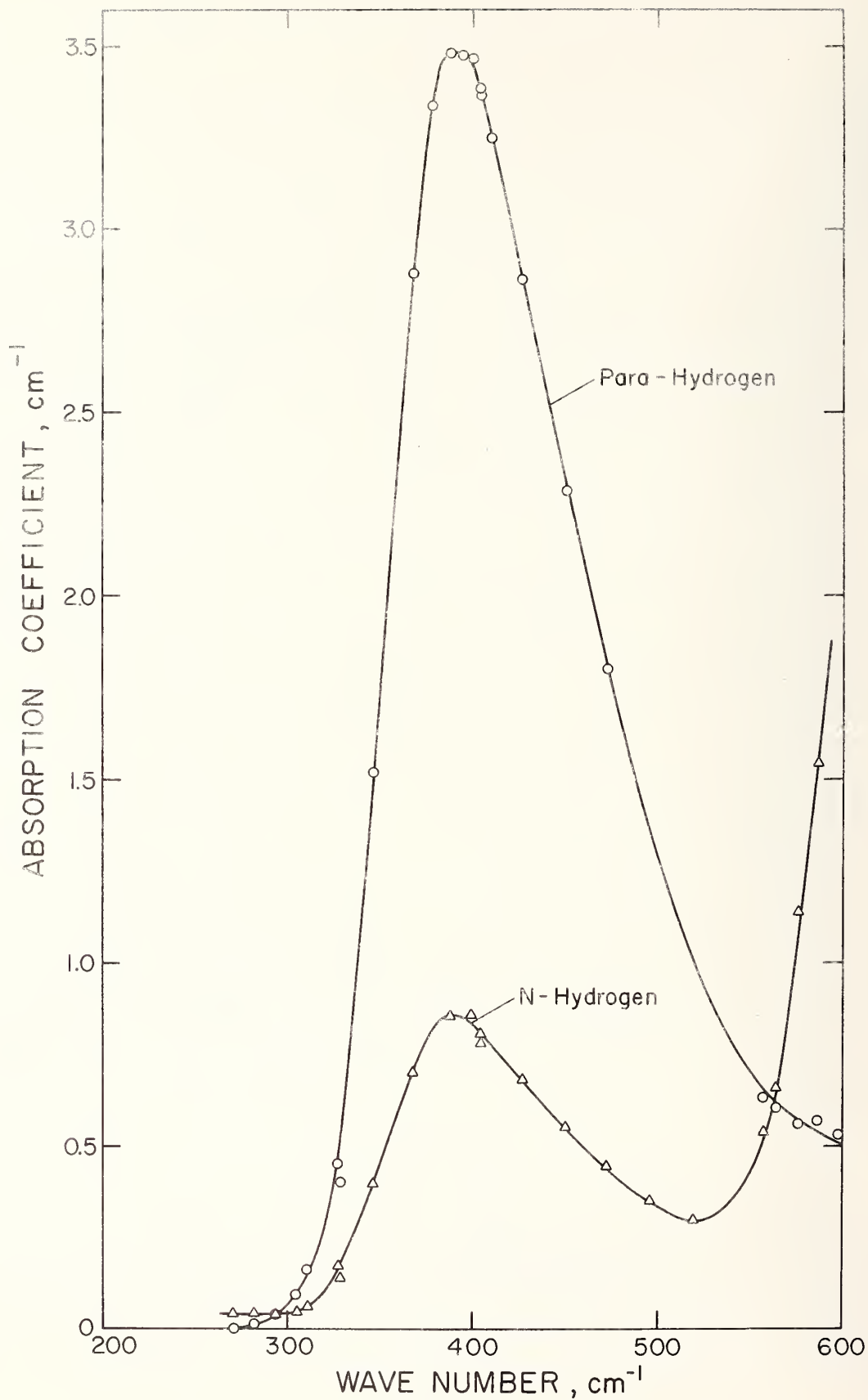


Figure 9. Far Infrared Absorption in Liquid Hydrogen-Rotational Band.

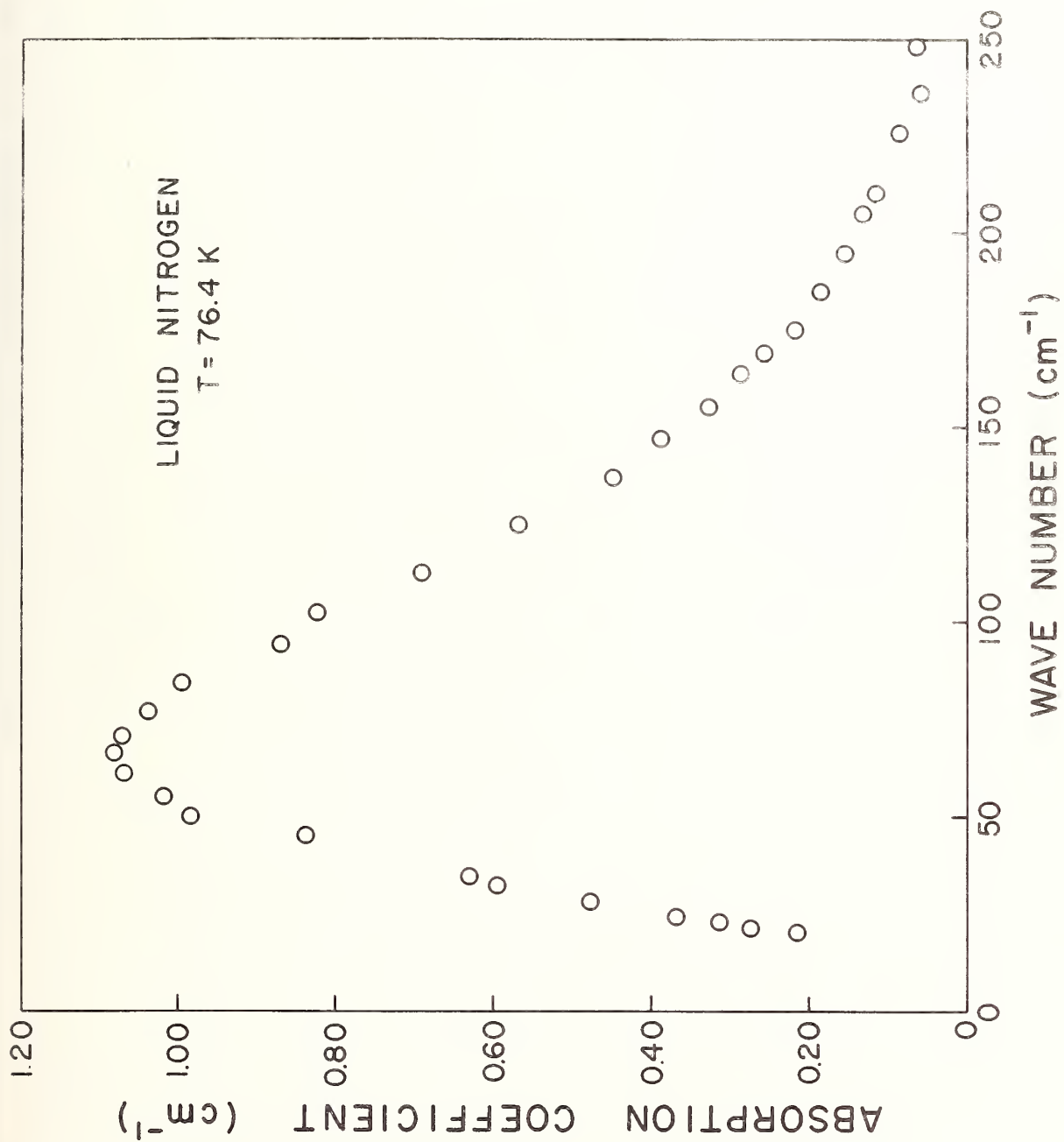


Figure 10. Far Infrared Absorption in Liquid Nitrogen.

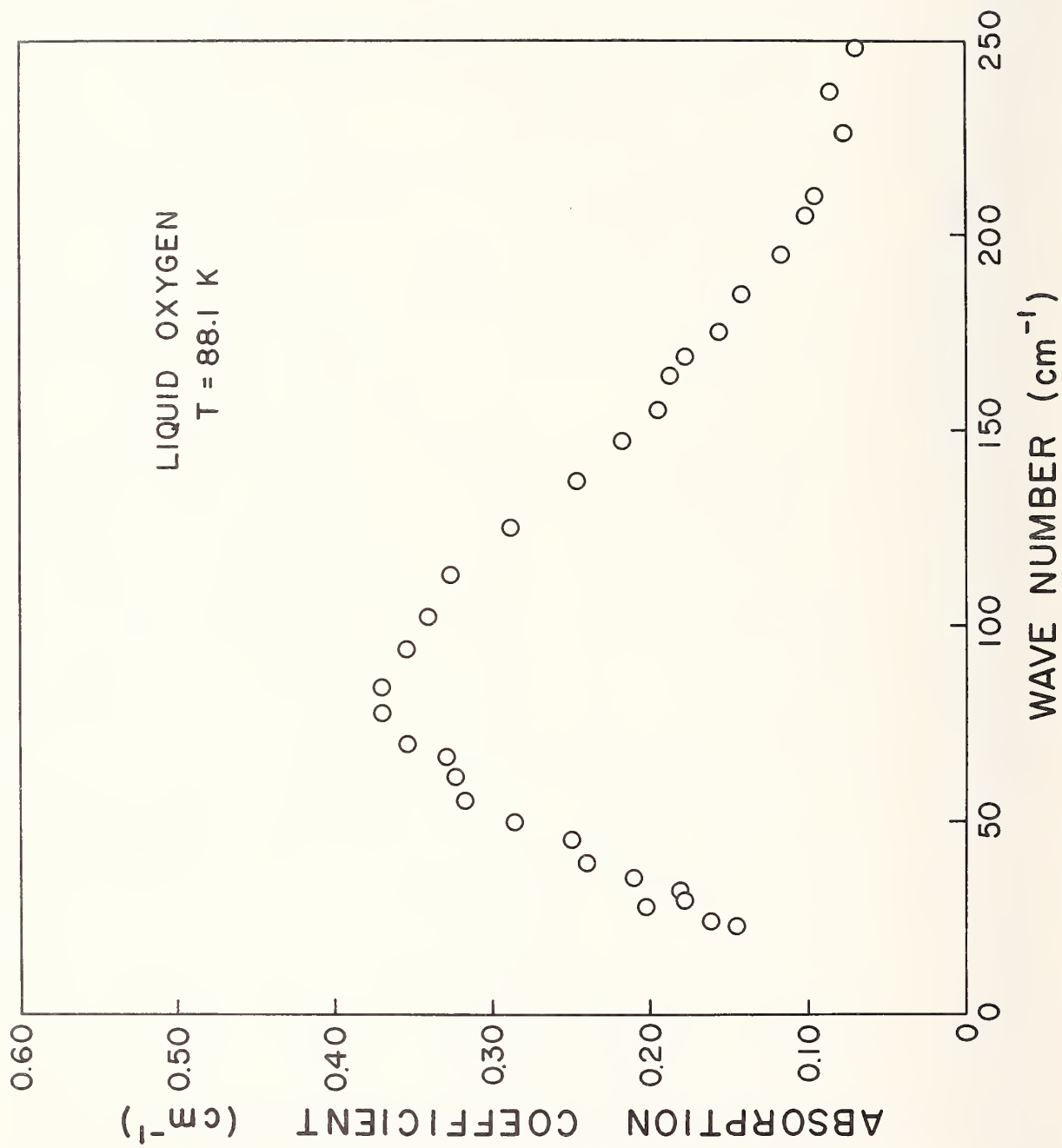


Figure 11. Far Infrared Absorption in Liquid Oxygen.

for our data. A possible explanation may lie in the difficulties mentioned by Stone and Williams in connection with the presence of ice crystals in their liquid samples. We too encountered such difficulties in earlier experiments which showed large absorption peaks at intervals over the entire spectrum. We feel that in the present data this problem has been entirely eliminated by the method of sample preparation described above.

The band is quite similar to that observed for compressed nitrogen gas (Bosomworth and Gush, 1965) for which a quadrupole-induced pure rotational origin is fairly well accepted. The broad rotational lines are more closely spaced than in the case of hydrogen (For the selection rule  $\Delta J=2$  these are  $8.0 \text{ cm}^{-1}$  and  $230 \text{ cm}^{-1}$  respectively) and a large number of them are superimposed to form a continuous band.

Bearing in mind the low density limitations of existing theory one can make a crude calculation of band shape based on the binary absorption coefficient. To do this one superimposes individual broadened lines of similar shape with relative intensities given, for example, by the formula of Colpa and Ketelaar (1958). We have done this using the asymmetric line shape suggested by Kiss and Welsh (1959) with a half width at half intensity of  $20 \text{ cm}^{-1}$  (Ketelaar and Rettschnick, 1964). The calculated band does not give a good fit at all frequencies but predicts the band maximum fairly well; we calculate  $60 \text{ cm}^{-1}$  compared to about  $65 \text{ cm}^{-1}$  from experiment.

#### 4.3 Liquid Oxygen

The spectrum of liquid oxygen, Figure 11, is quite similar to that of liquid nitrogen. However, the peak absorption coefficient is only 1/3 of that for nitrogen and the width of the band is greater. This difference was also noted by Bosomworth and Gush (1965) for the compressed gases. They point out that the difference is related to the weaker

quadrupole moment of the oxygen molecule and the resultant weaker induced dipole moment. In Table I the quantity  $Q\bar{\alpha}/\sigma^4$  is listed for different molecules. Here  $Q$  is the quadrupole moment,  $\bar{\alpha}$  the mean polarizability and  $\sigma$  the molecular diameter parameter of the Lennard-Jones potential function. This quantity is a useful measure of the induced dipole moment and the relative magnitudes of the absorption coefficient in figures 10 and 11 are in accord.

An explanation is demanded by the presence of a permanent magnetic dipole moment for oxygen, also listed in Table I. Rotational spectra in this wavelength region have been observed in the low pressure gas (Gebbie et al 1969) and attributed to magnetic dipole transitions. From the value given in Table I one might expect the resulting absorption coefficient in the liquid to be even greater than that shown for nitrogen in figure 10. But in fact these magnetic dipole rotational transitions are "approximately forbidden" and the value of the magnetic dipole itself does not tell the complete story; in order to observe them Gebbie et al used a path length of 180 m and the pure oxygen gas pressure was 3 atm. Assuming linearity of intensity with density the equivalent liquid path would be about 600 mm compared to 25.4 mm used here. Thus the magnetic dipole transitions appear to give only a minor contribution in figure 11. Similarly, in Gebbie's measurements the collision-induced transitions would have contributed only a minor part of the intensity because this part varies as the square of the density.

An envelope was again calculated as for nitrogen, but here a half width of  $50 \text{ cm}^{-1}$  was required in order to obtain a maximum at the observed frequency of  $80 \text{ cm}^{-1}$ .



Table I.

Comparison of induced and permanent dipole moments.

Quadrupole Moment, Q 10 <sup>-26</sup> esu	Mean Polarizability, $\bar{\alpha}$ 10 <sup>-25</sup> cm <sup>3</sup>	Lennard-Jones Force Constant, $\sigma$ 10 <sup>-8</sup> cm	Induced Dipole, $\mu = \frac{Q\bar{\alpha}}{\sigma^2}$ 10 <sup>-18</sup> esu		Permanent Dipole, $\mu$ 10 <sup>-18</sup> esu	Rotational Constant, B <sub>e</sub> cm <sup>-1</sup>
H <sub>2</sub>	0.63		7.9	2.968	0	60.8
N <sub>2</sub>	1.5		17.6	3.681	0	2.01
O <sub>2</sub>	<0.55		16.0	3.433	0.0185**	1.45
CO	1.6		19.5	3.590	0.112	1.93
CH <sub>4</sub>	0		26.0	3.822	0	5.2

\* Calculated from the octopole moment,  $\Omega = 3.7 \times 10^{-34}$  esu., i.e.,  $\mu = \frac{\Omega\bar{\alpha}}{\sigma^5}$

\*\* Permanent magnetic dipole of 2 Bohr magnetons.

Hirschfelder, et.al., (1964).

Herzberg (1950).

Nelson, et.al., (1967).

Spurling, et.al., (1968).

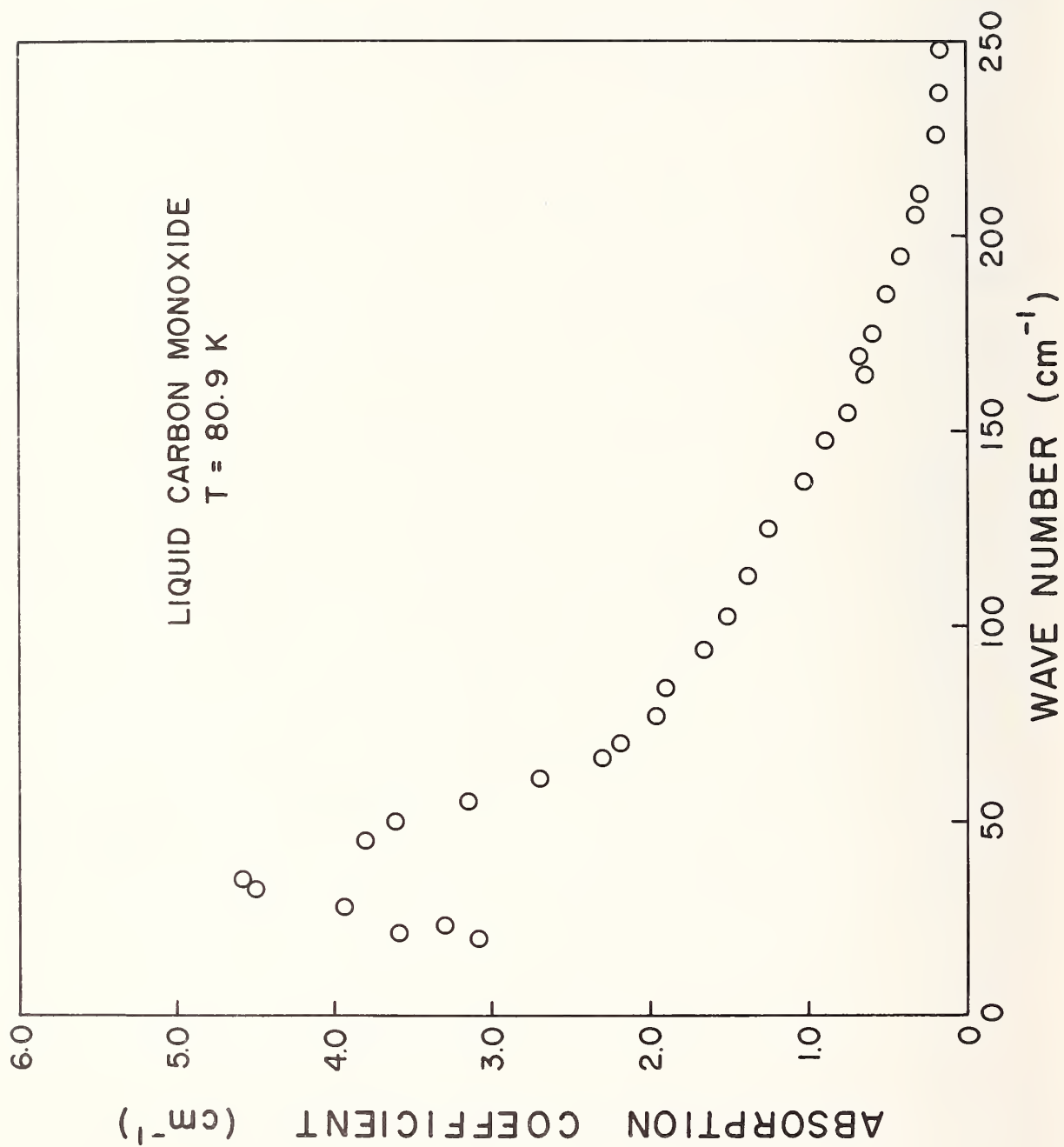


Figure 12. Far Infrared Absorption in Liquid Carbon Monoxide.

#### 4.4 Liquid Carbon Monoxide

The far infrared spectrum of liquid carbon monoxide, Figure 12, is composed of a sharp peak superimposed on a diffuse background. The carbon monoxide molecule is similar to the nitrogen molecule in that it has the same mass and the same number of electrons. In fact the molecular constants important in collision induced absorption are also similar as seen from Table I. It is thus to be expected that the spectra would also be similar, as indeed they are toward the higher frequencies. The existence of a small permanent dipole moment for CO, however, is considered to be the source of the only major difference: i.e., the sharp low frequency peak. However, even this small permanent dipole moment is an order of magnitude larger than the quadrupole-induced dipole and its effect should dominate that of the induced dipole moment. This can be seen from Table I. On account of this permanent dipole moment pure rotational absorption must take place according to the selection rule  $\Delta J=1$  in addition to  $\Delta J=2$  from the induced dipole. For this process, one can calculate the relative intensities of the rotational lines (Herzberg, 1950) to find the position of peak absorption. For liquid CO at 80.9 K we find the transition from  $J=6$  to  $J=7$  the most intense. The corresponding frequency is  $27 \text{ cm}^{-1}$  in fair agreement with the value of  $35 \text{ cm}^{-1}$  from figure 12.

#### 4.5 Liquid Methane

The spectrum for liquid methane is presented in figure 13. Some comment on this spectrum is called for because the methane molecule has neither permanent dipole nor quadrupole moment by virtue of its tetrahedral symmetry. The lowest order multipole allowed by symmetry is the octopole and this has been calculated from theory

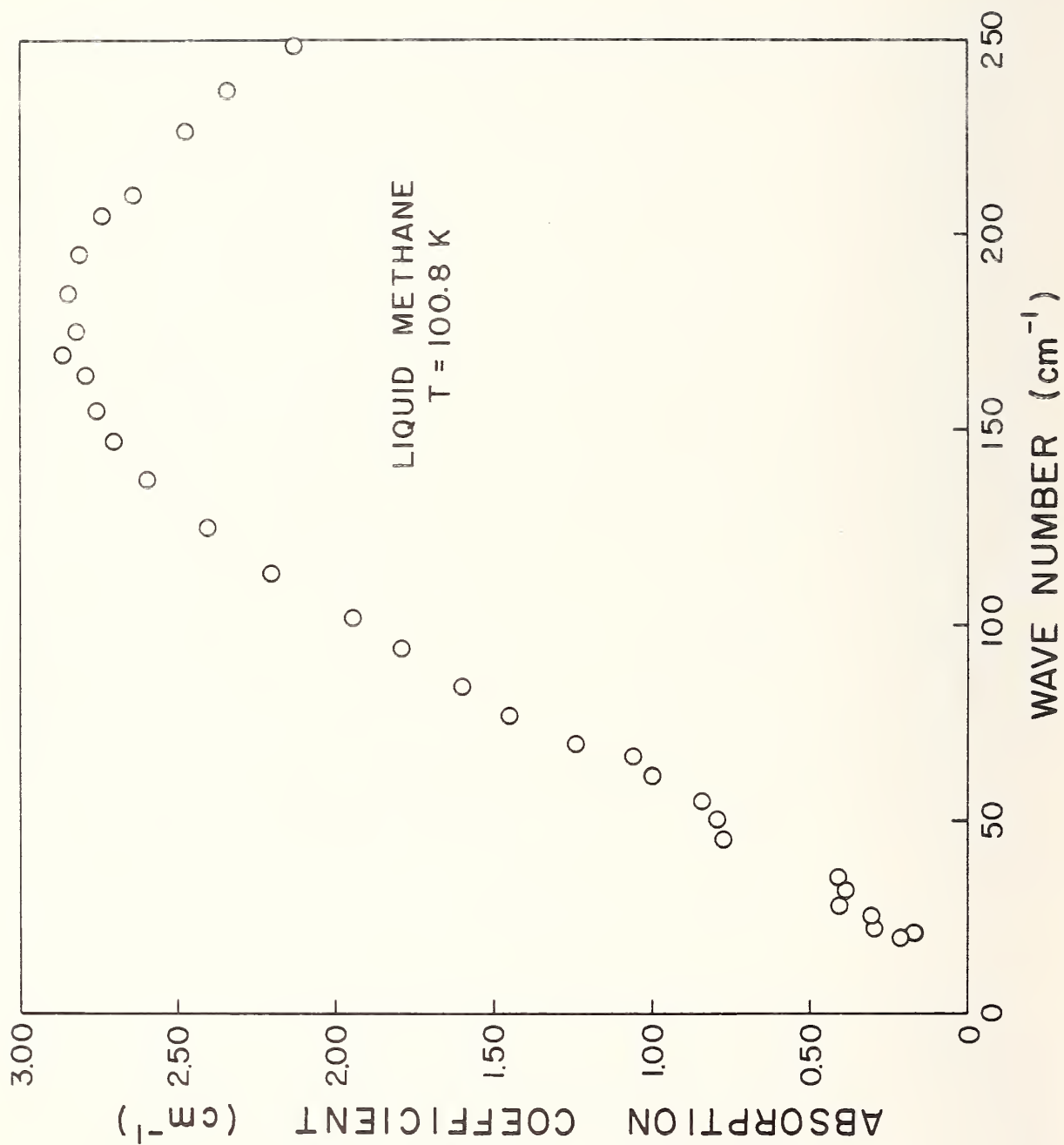


Figure 13. Far Infrared Absorption in Liquid Methane.

and from experimental second virial coefficients (Spurling, et. al., 1968). An order of magnitude estimate of the octopole-induced dipole moment at the point of closest approach of two molecules can be made from the quantity  $\Omega\bar{\alpha}/\sigma^5$  (see Table I). The results would lead one to expect pure rotational absorption intensities comparable to those observed for nitrogen and thus we conclude that it is entirely feasible that the spectrum arises primarily from collision octopole-induced pure rotational transitions.

Since our measurements were completed the far infrared spectrum of compressed methane gas at room temperature has been published by Birnbaum and Rosenberg (1968) who have calculated the octopole moment from their data. Their spectrum is similar in form to ours but as would be expected for pure rotation at a higher temperature it is more intense and the maximum is at a higher frequency.

#### 4.6 Liquid Argon

At wave numbers below  $250\text{ cm}^{-1}$  no significant difference could be observed in the transmission through path lengths of 4.1 mm and 25.4 mm. We conclude that compared with the other five liquids studied the absorption coefficient is negligible. This is in accord with the findings of Kiss and Welsh (1959) for compressed noble gases at room temperature and up to 180 atm. pressure and wave numbers greater than  $300\text{ cm}^{-1}$ . It is also in accord with the theory of induced absorption (Poll and van Kranendonk, 1961); no induced dipole can result from the collision of identical noble gas atoms.

### 5. APPLICATIONS-ABSORPTION OF THERMAL RADIATION

From a practical point of view it is of interest to be able to describe the absorption of thermal radiation in a liquid or dense vapor. Unfortunately this becomes involved with system parameters related

to the sources of radiation. However to illustrate how this might be done in a typical case we calculate here the modified Planck mean absorption coefficient (Sparrow and Cess, 1966) defined as

$$K_P(T_F, T) \equiv \frac{\int_0^{\infty} \alpha(n, T_F) I_b(n, T) dn}{\int_0^{\infty} I_b(n, T) dn}$$

Here  $n$  is the wave number and  $I_b(n, T)$  is the black body spectral intensity for temperature  $T$ . This quantity is the correct mean absorption coefficient in optically thin conditions for incident black body radiation of temperature  $T$  when the fluid is at temperature  $T_F$ . The quantity calculated when  $T = T_F$  is the Planck mean absorption coefficient and is seen to be a property of the fluid alone; i.e., contains no system parameters. However, this quantity is only of interest in emission, and, in the present, case at low temperatures is of little use. The modified coefficient as defined here contains only one system parameter,  $T$ .

For a typical problem we take  $T = 300$  K and calculate  $K_P(20$  K, 300 K) for liquids para and normal hydrogen. To do this with the data of figures 7 and 8 it is necessary to make an extrapolation on the high frequency side. We have determined that the high frequency side of the para-hydrogen  $J=0$  line is representable by the Lorentz line profile within experimental error as has been observed frequently in connection with rotational lines. Thus we have extrapolated using the relation

$$\alpha(n) = \frac{b^2 \alpha_{\max}}{(n - n_0)^2 + b^2}$$



where  $\alpha_{\max}$  is the maximum value of the absorption coefficient at the line center,  $n_o$ , and  $b$  is the half width ( $86 \text{ cm}^{-1}$ ). For normal hydrogen we have had to estimate  $\alpha_{\max}$  for the  $J=1$  line, the peak of which was not observable in our experiments. We have taken the same ratio for the  $J=1$  line to the  $J=0$  line as observed by Kiss, i.e., 1.88:1. The integrals were evaluated numerically and were carried to a high enough wave number that the residual contribution became negligible.

For para-hydrogen we calculate  $K_P = 0.53 \text{ cm}^{-1}$  and for normal hydrogen  $K_P = 0.40 \text{ cm}^{-1}$ . Thus for para-hydrogen 63% of the radiation is absorbed in a path length of 1.9 cm, while for normal hydrogen the same absorption occurs in a path length of 2.5 cm. It will be appreciated that for oxygen, nitrogen and carbon monoxide absorption of thermal radiation will be considerably less since only a narrow wave number region is covered by the observed spectra. Liquid methane on the other hand would appear to be an intermediate case. It is interesting to note that the fundamental band of liquid hydrogen in the range  $4000 - 5000 \text{ cm}^{-1}$  only accounts for at most 3 parts per million of the 300 K black body radiation and is thus of negligible importance in radiative transfer from such a source compared to the far infrared band described here.

## 6. CONCLUSIONS

We have measured the far infrared absorption coefficient of six cryogenic liquids at temperatures close to their normal boiling temperatures. A variety of behavior was found which could be mostly related to the molecular constants which determine the induced electric dipole moment. No theoretical relationship is available to calculate the absorption coefficient at liquid densities, but the data as such should be useful in applications such as the calculation of absorption of thermal

radiation. As an example of this the modified Planck mean absorption coefficient was calculated for normal and para-hydrogen and a 300 K source.

## 7. ACKNOWLEDGMENTS

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